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HIGH PRESSURE COSMOCHEMISTRY APPLIED TO  
MAJOR PLANETARY INTERIORS: EXPERIMENTAL STUDIES

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SUMMARY

The overall objective of this project is to determine the properties of the  $H_2$ -He- $H_2O$ - $NH_3$ - $CH_4$  system and related small-molecule systems that are needed to constrain theoretical models of the interiors of the major planets. This project is one of the first attempts to measure phase equilibria in binary fluid-solid systems in diamond anvil cells and, in that respect, represents a major advance of the art of high-pressure experimentation. Vibrational spectroscopy, direct visual observations, and x-ray diffraction crystallography of materials confined in externally heated cells are our primary experimental probes. We also are measuring adiabats in these systems in order to constrain models of heat flow in these bodies and to detect phase transitions by thermal anomalies. Other studies are directed toward (1) interpreting high pressure reactions in these systems that are suggested by shockwave measurements and (2) developing methods for reaching high temperatures and high pressures of planetary interest in diamond cells.



**Detailed Description of Work in Progress During the Period 11/1/84-4/30/85**

Dr. Johnson's principal task continues to be to extend our determinations of the phase diagram of  $(\text{NH}_3)_x(\text{H}_2\text{O})_{1-x}$  at compositions in the range  $0 \leq x \leq 0.5$ , pressures up to 4 GPa, and temperatures from 100 to 400 K. Earlier work on this task has been described in previous reports. Among other tasks undertaken during this reporting period, Dr. Johnson set up the new variable temperature chamber for the diamond-anvil cell and new microscope system and used this equipment to check the phase diagram of water from -26 to 100° C to 5.5 GPa. With this equipment, ices VI, VII, and VIII could be clearly distinguished from the liquid and from each other. Ice III also may have been detected. Thus, a major difficulty with our previous equipment has been overcome. Dr. Johnson also refined somewhat the system for loading high ammonia samples in order to improve our ability to prepare solutions with accurately known concentrations. Work on the phase diagram will continue during the spring.

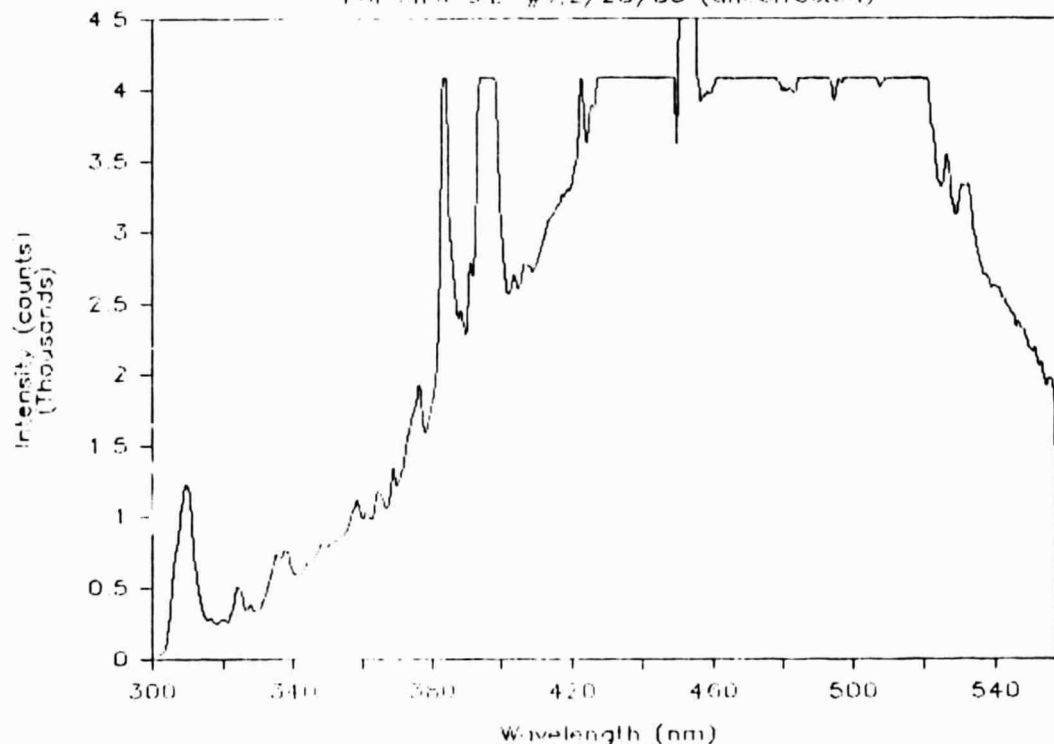
Much of the remainder of Dr. Johnson's efforts were devoted to a shockwave study of the equations of state of simple C-H-N-O molecules. Previous shock wave work by Nellis, Holmes and co-workers at the Lawrence Livermore National Laboratory have produced data about high pressure properties of the "gases" of planetary interest which suggest that many "gases" undergo chemical transformations at pressures between 12 and 100 GPa. Until recently, products of these reactions have not been identified. Under auspices of the University of California Institute of Geophysics and Planetary Physics Branch at Livermore, Professor Nicol and Dr. Johnson are collaborating with the Livermore group to analyze the products by detecting molecular emission spectra during passage of the shock front. The experiments are conducted at Livermore's two-stage light gas gun facility.

Room-temperature benzene samples were used for feasibility studies in order to avoid the inconveniences of cryogenic targets. More than a dozen shots were fired at pressures from 20 to more than 50 GPa and temperatures estimated to range from 2000 to 5000 K during one nine-day period in February and two shorter sessions in April. During each shot, visible and near ultraviolet emission spectra were collected with one or two gated, intensified optical multichannel analyzers during a 50-to-100 nsec period while the shock front passed through the focal plane of the collection optics. In some of the earlier shots, some data were lost as a result of (1) triggering problems and (2) detector saturation (for example, the 440-to-530 nm region of Fig. 1.). However, many shots have now been a number of bands characteristic of  $\text{C}_2$  (near 468, 515, and 555 nm, for example), CH (near 395 and 430 nm among other possibilities) and of other small molecules were readily detected above the thermal "grey-body" background over a wide range of pressures (Fig. 1-3).

These results are now being analyzed and will be described in invited presentations at the AIRAPT Conference (Amsterdam, July), and the Symposium on Shock-Initiated Chemistry at the Fall ACS Meeting (Chicago, September) and at the APS Topical Conference on Shock Phenomena (Spokane, July).

## Benzene Emission Spectrum

For shot S.E. #9, 2/28/85 (uncorrected)



**Figure 1. Emission spectrum (300-550 nm) obtained of benzene shocked to 58 GPa with detector A at high sensitivity and f.4 optics during shot #9. At this sensitivity, this detector saturates at the 40% count level; the spike near 460 nm is an artefact of the gating circuits. The strong uv peaks near 396, 384, and 310 nm that are believed to be features of the spectrum of CH. (This spectrum is not corrected for the spectral sensitivity of the detector.)**

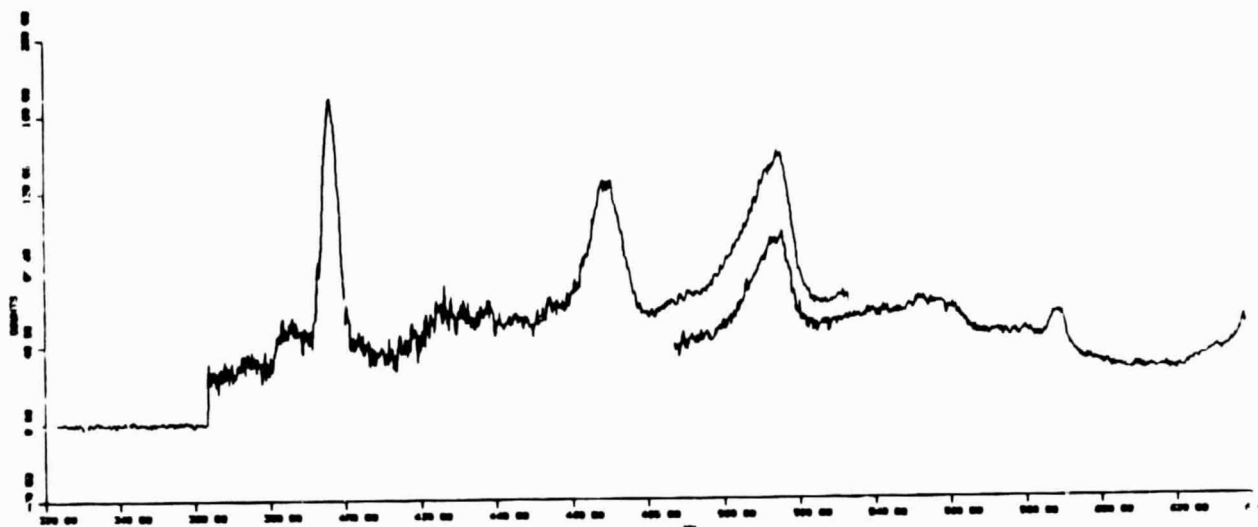


Figure 2. Emission spectra (a: 364-535 nm; b: 475-640 nm) of benzene shocked to (a) 40 and (b) 24 GPa obtained with detector B and f.4 optics during shots #10 and #11. Bands near 470, 510, and 560 nm appear in many spectra and are attributed to excited states of  $C_2$  produced during benzene decomposition. The 396, 384, and 340-nm features also are evident in Figure 1. The 586-nm feature is attributed to Na impurities. The resolutions of these spectra were limited by the detector slit widths.

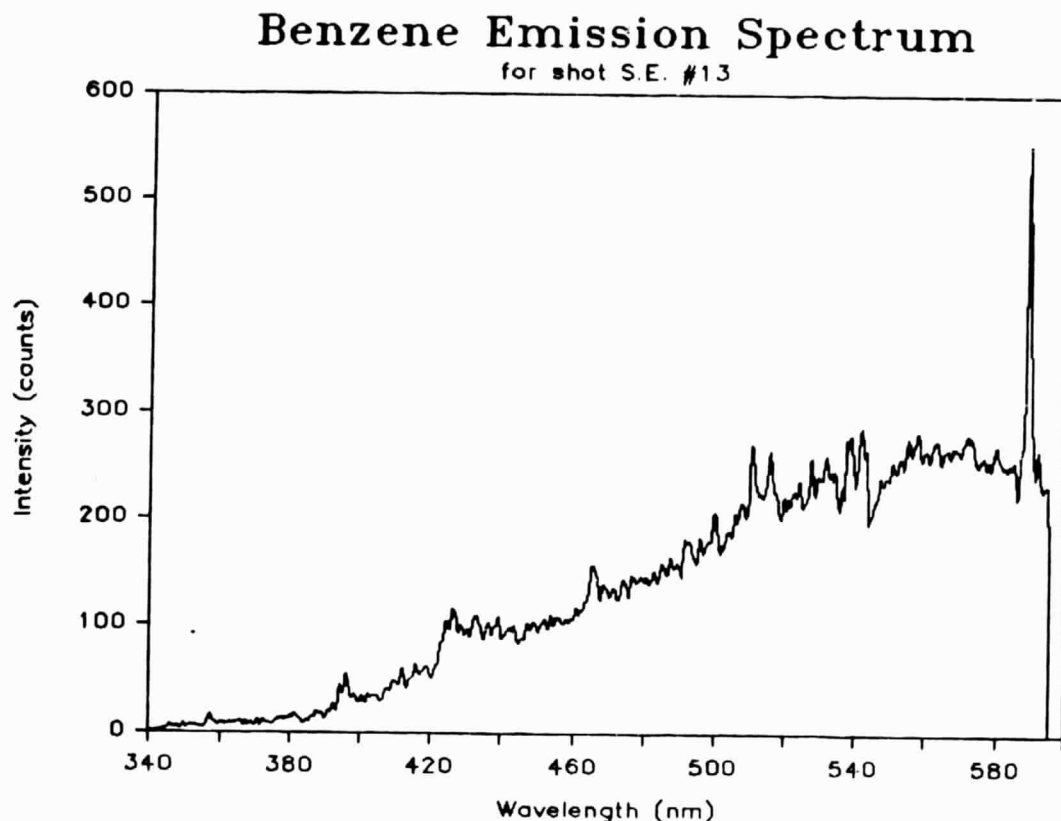


Figure 3. Emission spectrum (340-590 nm) obtained of benzene shocked to 29 GPa with detector A at low sensitivity and f.10 optics during shot #13. The dip near 545 nm is an artefact of the gating circuits. Most of the features also are seen in Figs. 1 and/or 2 but with different intensities. (This spectrum is not corrected

Further experiments are tentatively scheduled for the Fall, when we intend to examine methane, carbon monoxide, and other light molecules of planetary interest and to determine whether other molecular products can be detected by laser excitation of the shocked material.

During the Spring, Professor Nicol and Dr. Reinhart Boehler developed techniques for resistively heating Fe, W, and other wires to their melting points in a gasketed diamond-anvil cell. Since Dr. Johnson had developed programs to fit grey and black body emission spectra in conjunction with the Livermore project, she was asked to modify these programs so that the OMA could be used to measure the temperatures of these hot wires. Thus, during April, she joined in a study of the pressure-temperature, current-voltage determination of the phase diagram of Fe by this technique. This work will be described in a paper to be presented at the May AGU meeting and a poster at the July AIRAPT conference.

In other developments, one of two high pressure cells for use with the Department of Chemistry and Biochemistry's cryogenic Huber four-circle x-ray diffractometer was delivered during April. Ms. Alexis Zinn, a B.S.-M.S. student supported by Dr. Nicol's NSF grant, is now working to adapting them to the diffractometer. We hope that the system will be operational during the Summer. Mr. C.S. Yoo, a Ph.D. candidate supported by grants from NSF and the California Space Institute, has completed the adaptation of the department's new FT infrared spectrometer for our high pressure cells so that we can routinely obtain infrared spectra of our high pressure samples. This will be used to identify new high pressure  $\text{NH}_3 \cdot \text{H}_2\text{O}$  phases.

Mr. Steven Boone is completing his second year of graduate work and has begun to measure adiabats of ammonia-water mixtures using the piston-cylinder press as permitted by his other commitments to course work, service as a teaching assistant, and other degree requirements. He has been awarded a NASA Graduate Student Research Fellowship for 1985-6 and will devote full time to this project. During that period, he plans to work with Dr. Reinhard Boehler to extend the adiabat studies to higher ammonia concentrations by developing special loading techniques for very volatile solutions that will prepare us for extending the measurements to mixtures of methane and water.

Bibliographic Data: Abstracts of five presentations to be made between May and September 1985 are appended; complete bibliographic citations are not available but will be included in the November 1985 report.

Abstract submitted for the American Geophysical Union Meeting,  
Baltimore, MD, May 1985

Internally Heated Diamond Anvil Cell: Melting of Iron.

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Physics and Department of Chemistry and Biochemistry,  
University of California, Los Angeles, CA 90024)  
CHANG-SHENG ZHA, MARY L. JOHNSON, and MALCOLM NICOL  
(All at Department of Chemistry and Biochemistry,  
University of California, Los Angeles, CA 90024)

Fine wires (0.001" in diameter) of iron or tungsten are heated resistively to their melting temperatures in a gasketed diamond anvil cell. The gasket consists of two stainless steel disks that act as electrical leads. Mica or vapor-deposited aluminum oxide electrically insulates the two gasket halves from each other. Sodium chloride and silica glass are used as pressure media. The pressure and pressure distribution are determined by the ruby scale; temperatures are measured by comparing the spectrum of the hot wire with the black body radiation of a standard lamp using an optical multichannel analyzer. Because the necessary electrical power is low (less than 10 watts at the melting temperature of tungsten), high temperature stability is obtained; and high quality spectra to over 3000° C are observed. Melting is determined from the discontinuity in the power-temperature function. Possibilities for using synchrotron x-ray sources to obtain high temperature equations of state are discussed.

Support for this work by DOE DE-AT 03-81 ER 10965 [RB, CSZ]; NSF EAR80-10827 [RB]; NASA NAGW-104 [MN, MEJ]; and NSF DMR83-18812 [MN] is greatly appreciated.



Abstract of an invited talk for the AIRAPT Conference  
Amsterdam, Netherlands - July 1985

TRIBOCHEMILUMINESCENCE SPECTRA OF SHOCK-DECOMPOSED BENZENE\*

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Shock and static high pressure studies suggest that benzene reacts during shock compression at pressures above 13 GPa. However, few products have been recovered; and the chemistry of the high pressure reactions has not been established. This report describes the first application of time-resolved (50-to-100 nsec) tribochemiluminescence (TCL) spectroscopy to detect intermediates during the decomposition reactions. At shock pressures of the order of 5 GPa, intense TCL bands characteristic of C<sub>6</sub> and C<sub>2</sub> species, among other features, are readily identified above the grey-body background. The spectroscopic techniques will be described, and the dependence of the TCL spectra on shock parameters will be discussed in terms of known decomposition mechanisms of highly excited benzene molecules.

\* Support provided by grants LLNL-IGPP-84-19 and NASA NAGW-104 and equipment provided by NSF DMR80-24620 are gratefully acknowledged.

Abstract of a poster presentation submitted to the AIRAPT Conference  
Amsterdam, Netherlands - July 1985

RESISTANCE HEATING OF Fe AND W IN DIAMOND-ANVIL CELLS\*

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Fine wires (25 micron in diameter) of iron or tungsten have been heated resistively to their melting temperatures in a diamond anvil cell that was gasketed with two stainless steel disks that acted as electrical leads. The two disks were electrically insulated from each other by mica, MgO, or vapor-deposited aluminum oxide; sodium chloride or silica glass were used as pressure media. The pressure and pressure distribution are determined by the ruby scale; temperatures are measured by comparing the spectrum of the hot wire with the black body radiation of a standard lamp using an optical multichannel analyzer. Because the necessary electrical power is low (up to 10 watts) high temperature stability is obtained; and high quality spectra from 600 to over 3000° C have been observed. Phase transitions and melting have been determined from discontinuities in the power-temperature function. Possibilities for using synchrotron x-ray sources to obtain high temperature equations of state will be discussed.

\*Support for this work by DOE DE-AT 03-81 ER 10965 [RB, CSZ]; NSF EAR80-10827 [RB]; NASA NAGW-104 [MN, MEJ]; and NSF DMR83-18812 [MN] is greatly appreciated.

Abstract of Invited Presentation for a  
Symposium on Shock-Initiated Chemistry  
at the Fall 1985 Meeting of the American Chemical Society  
Chicago, Illinois - September 1985

ANALYSIS OF BENZENE SHOCK-DECOMPOSITION CHEMISTRY BY EMISSION SPECTROSCOPY.\*

Malcolm Nicol and Mary L. Johnson, Department of Chemistry and Biochemistry,  
University of California, Los Angeles, CA 90024 and Neil C. Holmes, University  
of California, Lawrence Livermore National Laboratory, Livermore, CA 94550

Benzene and many other carbon compounds decompose when subjected to shock pressures in excess of 10 GPa, but little information is available from either in situ or recovery studies about the products of these high pressure decomposition reactions. We have recently identified some of the initial molecular decomposition products by means use of time-resolved (50-to-100 nsec) chemiluminescence spectroscopy. When liquid benzene is shocked to pressures from 15 to 60 GPa, bands of the C<sub>2</sub> spectrum are found among other atomic and molecular features and a grey-body background. The spectroscopic techniques will be described, and the dependence of the spectra on shock parameters will be discussed in terms of known decomposition mechanisms of highly excited benzene molecules.

\* Support provided by grants LLNL-IGPP-84-19 and NASA NAGW-104 and equipment provided by NSF DMR80-24620 are gratefully acknowledged.

Abstract Submitted for the  
APS Topical Conference on Shock Waves in Condensed Matter  
Spokane, Washington - July 1985

Molecular Emission From Shock-Decomposed Benzene. M. NICOL and M.L. JOHNSON, UCLA and N.C. HOLMES, LLNL.<sup>\*</sup>--Benzene and many other carbon compounds are known to decompose when shocked to pressures in excess of 10 GPa; however, few products of these high pressure reactions have been identified by either in situ or recovery methods. In this report, we discuss the use of time-resolved (50-to-100 nsec) chemiluminescence spectroscopy to identify excited molecular products of such decompositions. With benzene at pressures from 20 to 60 GPa, for example, intense spectra characteristic of C<sub>2</sub> are readily identified among other features and a grey-body background. The spectroscopic techniques will be described, and the dependence of the spectra on shock parameters will be discussed in terms of known decomposition mechanisms of highly excited benzene molecules.

<sup>\*</sup> Support provided by LLNL-IGPP-84-19, NASA NAGW-104 and NSF DMR80-24620 is gratefully acknowledged.